

In Situ X-ray Absorption Studies of Cathode Materials for Rechargeable Lithium-Ion Batteries

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Rechargeable batteries with high energy and power density are in great demand as energy sources for various purposes; e.g., portable telecommunication, computer equipment, hybrid electric vehicles, etc. Lithium-ion batteries are the most promising candidates to fulfill such needs due to their intrinsic high discharge voltage and relatively light weight. The current commercial lithium-ion battery is based on a LiCoO_2 cathode and a graphitized anode¹. LiCoO_2 is an excellent cathode material, with good capacity, reversibility and charge/discharge rate capability. However, due to the high cost of Co there has been a considerable interest in developing cathode materials based on Mn, V, or Ni. The key attributes required for a successful cathode material are: (1) a high intercalation potential (the voltage at which the material exchanges lithium), (2) a high lithium ion capacity (at least one lithium reacting per transition metal atom), (3) fast lithium ion diffusion kinetics (to allow high-rate cycling) and (4) complete chemical reversibility during repeated cycling (most easily attained if the crystal structure does not change drastically during lithiation/delithiation). Attributes (1) and (2) determine the energy density, (3) determines the power density and (4) determines the rechargeability and cycle life of the battery. In order to help design cathode materials with these attributes, it is of fundamental importance to understand the changes in the structural and electronic properties of the cathode materials during electrochemical cycling. *In situ* x-ray diffraction plays a vital role in elucidating the long-range structural changes that accompany lithiation/delithiation². In this report we highlight some of our recent results and findings, using *in situ* x-ray absorption spectroscopy (XAS), on the electronic and atomic structure of nickel/manganese oxide-based cathode materials. The element specific nature of XAS, its dependence only on the short-range order and its sensitivity to dilute elements make it an ideal tool to study this class of materials. The XAS experiments were performed at beamline X11A. All experiments were performed *in situ* using a specially designed spectro-electrochemical cell³. The cell pack consists of the cathode, a Li foil anode, a Celgard separator and electrolyte (1 M LiPF_6 in an ethylene carbonate-dimethyl carbonate solvent). The cell was housed between two blocks of aluminum, machined to provide win-

dows for the passage of x-rays and holes for bolts. The windows were sheets of 250 μm thick mylar. A rubber gasket was used to make a hermetic seal. Provisions were made for current collection by using thin copper and aluminum strips. The cells were assembled in an argon-filled glove box.

Nickel oxide-based systems

LiNiO_2 has been considered as a candidate to replace LiCoO_2 as a cathode material. Both LiNiO_2 and LiCoO_2 have a similar layered structure (prototype: $\alpha\text{-NaFeO}_2$). The structure is illustrated in Fig. 1. LiNiO_2 has a high initial capacity of 200 mAh g^{-1} under normal cell operating conditions. However, a major problem is that, in contrast to LiCoO_2 , it is difficult to prepare stoichiometric LiNiO_2 reproducibly. This non-stoichiometry is associated with a Li deficiency and the presence of Ni^{2+} ions in the lithium layers. These Ni ions interfere with the mobility of Li ions. There is also evidence that with a high degree of Li deintercalation, Ni ions migrate from Ni to the Li layers. Partial substitution of Ni by Co greatly stabilizes the LiNiO_2 structure and decreases the deviation from stoichiometry. Also, addition of small amounts of other elements such as Mg and Ga (< 2%)

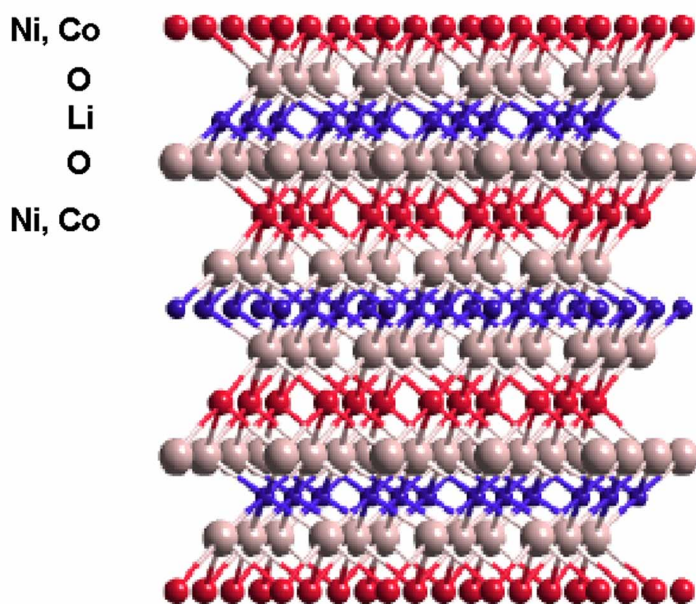


Figure 1. The layered structure of LiNiO_2 and LiCoO_2 (prototype: $\alpha\text{-NaFeO}_2$).

has shown to improve the chemical stability and cycling behavior of the electrodes. We have performed an *in situ* XAS study to investigate the evolution of the local electronic and atomic structure of $\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$ and $\text{LiNi}_{0.908}\text{Co}_{0.085}\text{Ga}_{0.003}\text{O}_2$ cathode material during electrochemical delithiation. The XAS spectra at the Ni and Co K-edges were obtained in the transmission mode while the Ga K-edge spectra was obtained using a 13-element Ge detector in the fluorescence mode. Figure 2 shows the near edge spectra (XANES) of Ni and Co in $\text{Li}_{1-x}\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$ ($0 \leq x \leq 1$) for a few representative values of x . On charging (delithiation), the Ni-edge shifts rigidly to high-energy values. By comparison with Ni standard compounds, we infer that in the fully lithiated state Ni is present in the Ni^{3+} oxidation

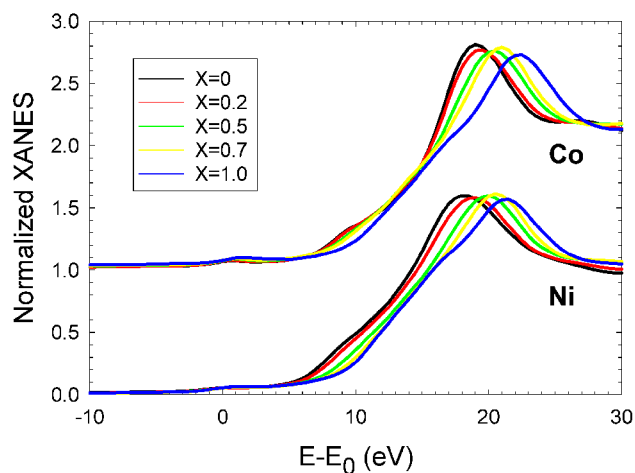


Figure 2. The XANES spectra of Co and Ni absorbers in $\text{Li}_{1-x}\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$ for various values of x .

state. On electrochemical delithiation the Ni ions oxidize during the initial stages of charge and attain a maximum oxidation state of Ni^{4+} close to the end of charge ($x=0.85$). In contrast, the Co XANES does not show any rigid shift in the edge position, indicating that the oxidation state of Co does not change during the initial stages of charge. Figure 3 shows the Fourier transform (FT) of the extended x-ray absorption fine structure (EXAFS) spectra for the Ni and Co absorbers. The first peak is due to Ni-O and Co-O interactions, respectively. It can be seen that for $x=0$, the amplitude of the Ni-O peak is much lower than that of Co-O. Ni^{3+} (low-spin d^7) is a Jahn-Teller active ion. Due to the Jahn-Teller effect, the Ni-O shell is split into two sub-shells (4 O at ~ 1.91 Å and 2 O at ~ 2.04 Å). Destructive interference from these two sub-shells leads to a reduced peak height in the case of Ni absorbers for $x=0$. Also, as the sample is delithiated the amplitude of the Ni-O peak increases while that of the Co-O peak remains almost the same. This increase in the

amplitude of the Ni-O peak is due to the creation of Ni^{4+} , which is not Jahn-Teller active. When all the Ni ions are oxidized to Ni^{4+} , the Ni ions are coordinated by a symmetric shell of 6 oxygen atoms at ~ 1.88 Å. This Ni-O bond distance is consistent with the value expected for a Ni^{4+} -O bond. EXAFS analysis clearly shows that in the fully lithiated state Co is surrounded by a symmetric shell of 6 oxygen atoms at ~ 1.91 Å. This is expected for a Jahn Teller inactive Co^{3+} ion. The Co EXAFS results are also consistent with a more or less random distribution of Co in the NiO_2 layers. Further details of the local atomic and electronic structure of the Ni and Co absorbers can be found in Ref. (4). Figure 4 shows the FT of dilute Ga dopants in $\text{LiNi}_{0.908}\text{Co}_{0.085}\text{Ga}_{0.003}\text{O}_2$ cathode material for various

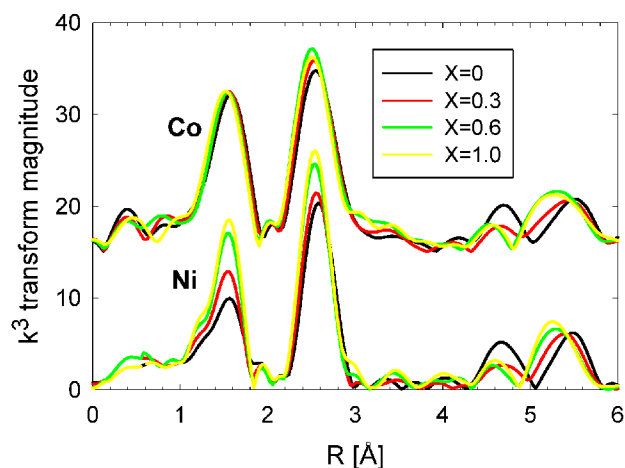


Figure 3. The Fourier transforms of the Co and Ni EXAFS in $\text{Li}_{1-x}\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$ for various values of x .

states of charge. The general appearance of the FT of the fresh electrode is very similar to that seen for Ni or Co atoms (Fig. 3). The first two peaks correspond to Ga-O and Ga-metal correlations. The FT's of the charged samples are distinctly different from that of the fresh electrode. This indicates that there are large local structural changes around the Ga ions on charging. Our results suggest that in the fresh electrode Ga^{3+} ions occupy regular octahedral Ni-type sites in the host lattice. Ga^{3+} ions are surrounded by 6 O neighbors at ~ 1.97 Å and 6 Ni neighbors at ~ 2.89 Å. On charging, the average Ga-O bond distance falls to ~ 1.87 Å and the coordination number falls to about 4.5. These findings clearly indicate that a majority of the Ga^{3+} ions (>65%) migrate to tetrahedral sites in the interstitial spacing. Also, in the charged state at least two distinct Ga-Ni bond distances, ~ 2.85 Å and ~ 3.27 Å are seen. We ascribe the shorter bond distance to the correlation between Ga ions that remain in octahedral Ni-type sites and Ni ions in the lattice, and the longer bond distance

to the correlation between Ga in tetrahedral sites and Ni ions in the regular lattice sites. We speculate that the migration of the Ga^{3+} ions suppress the transfer of Ni to Li-type sites and also helps to maintain a single hexagonal phase by acting as pillaring ions during high states of charge. We suggest that the high stability of Ga in tetrahedral sites is at the origin of the significant improvement of the cycling and structural properties of Ga-doped cathode materials reported earlier by others⁵.

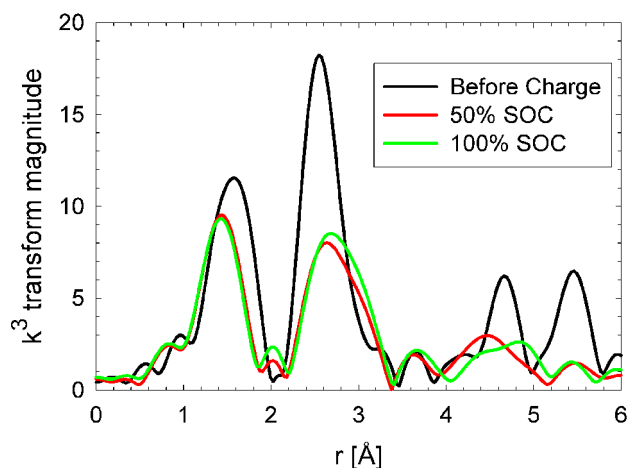


Figure 4. The Fourier transforms of the EXAFS of dilute Ga dopants in $\text{LiNi}_{0.908}\text{Co}_{0.085}\text{Ga}_{0.003}\text{O}_2$ for various states of charge.

Manganese oxide-based systems

Due to the relative abundance of Mn there has been a considerable interest in developing Mn-oxide based cathode materials. The spinel $\text{Li}_x\text{Mn}_2\text{O}_4$ ($0 \leq x \leq 2$) has been considered as a cathode material. However, due to the cooperative Jahn-Teller distortion exhibited by Mn^{3+} the material undergoes a cubic to tetragonal phase transition for $x > 1.1$. This results in rapid degradation of the electrode. Several researchers have developed layered- LiMnO_2 . However, layered- LiMnO_2 is metastable and transforms to spinel LiMn_2O_4 on cycling. More recently, Davidson's group at the National Research Council, Ottawa have shown that substitution of lithium for up to 20% of the transition metal atoms in $\text{LiCr}_y\text{Mn}_{1-y}\text{O}_2$ -type materials improves the electrochemical characteristics⁶. The layered structures in $\text{Li}[\text{Li}_x\text{Cr}_y\text{Mn}_{1-x-y}]\text{O}_2$ phases are stabilized by the partial or complete oxidation of the Mn to the +4 oxidation state. In collaboration with Davidson's group we have investigated the redox mechanism and the local structure of $\text{Li}(\text{Li}_{0.2}\text{Cr}_{0.4}\text{Mn}_{0.4})\text{O}_2$ cathode material using *in situ* transmission Cr and Mn XAS. This cathode material has a high capacity of about 200 mAh g^{-1} with good rate capability and cyclability.

Even on extended cycling, the deleterious spinel LiMn_2O_4 is not formed. Figure 5 illustrates the Cr XANES of representative scans during delithiation. On delithiation the Cr edge position shifts to higher energy values and the shape of the spectra change significantly. In particular, the pre-edge region shows the gradual appearance of a strong peak (enlarged in the inset). In tetrahedrally coordinated Cr-oxide compounds a significant pre-edge peak, attributed to a bound $1s \rightarrow 3d$ transition, is seen. These observations show the oxidation of Cr^{3+} to Cr^{6+} on delithiation. By comparing with data on Cr standards we estimate that about 40% of the Cr^{3+} ions are converted to Cr^{6+} ions at the end of charge. In sharp contrast, the Mn XANES shows only minor changes in shape and no systematic shift in edge position, indicating no change in oxidation state of Mn. Thus, charge compensation can be largely ascribed to the oxidation of octahedral Cr^{3+} to tetrahedral Cr^{6+} on delithiation. The creation of Cr^{6+} is also clearly visible in the Cr EXAFS and is illustrated in the FT's shown in Fig. 6. The first two peaks of the as-prepared electrode are due to Cr-O (6 at ~ 1.97 Å) and Cr-Cr/Mn (6 Cr-metal at ~ 2.88 Å) correlations. On delithiation the amplitude of both the Cr-O as well as Cr-metal peaks decrease. Typically, Cr^{6+} -O bond distance tends to be ~ 1.65 Å and Cr^{3+} -O bond distance ~ 1.98 Å. Due to this distinct difference in the bond distances, the electronic waves from the Cr^{3+} -O and Cr^{6+} -O pairs are out of phase for a significant portion of the k-range of the EXAFS signal. This accounts for the decrease in the Cr-O peak

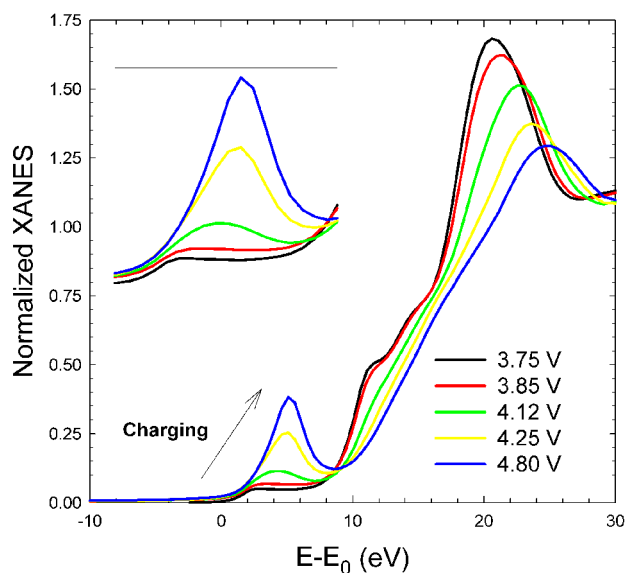


Figure 5. The XANES of Cr absorbers in a Cr-Mn based cathode material for representative states of charge. The state of charge of the cathode increase with increasing voltage.

intensity in the FT's on delithiation. As the regular Cr^{3+} sites are of octahedral symmetry, conversion to Cr^{6+} leads to the migration of Cr to interstitial tetrahedral sites; leaving behind vacancies in the regular octahedral sites. The formation of these vacancies leads to the decrease in the peak height of the Cr-metal correlations. EXAFS analysis suggests that in the fully charged state about 43% of the Cr ions exist as Cr^{6+} in tetrahedral sites and the rest remain as Cr^{3+} in regular octahedral sites. This finding is consistent with the results of the XANES measurements. In contrast, the Mn EXAFS suggest that for all states of charge, Mn is surrounded by 6 O at $\sim 1.89 \text{ \AA}$ and by 4 Cr/Mn atoms at $\sim 2.87 \text{ \AA}$. The Mn-O bond distance of 1.89 \AA is in agreement with the value expected for a Mn^{4+} -O bond. However, note that for all states of charge only 4 Mn/Cr atoms surround Mn (unlike Cr ions, which are surrounded by 6 Mn/Cr neighbors in the as prepared material). Also, the creation of vacancies in the lattice due to movement of Cr from octahedral sites to tetrahedral sites does not create a lower number of Mn/Cr neighbors around Mn absorbers. These observations suggest that the excess Li atoms cluster preferentially around the Mn ions (Li has a very small backscattering amplitude and cannot be easily detected) and that on a local scale the sample is inhomogeneous with Cr and Mn-rich domains. The local structure of Cr and Mn are similar to that found in LiCrO_2 and Li_2MnO_3 [$\text{Li}(\text{Li}_{1/3}\text{Mn}_{2/3})\text{O}_2$], respectively. The reversibility of the charge-discharge process was further studied by *in situ* XAS. Cr

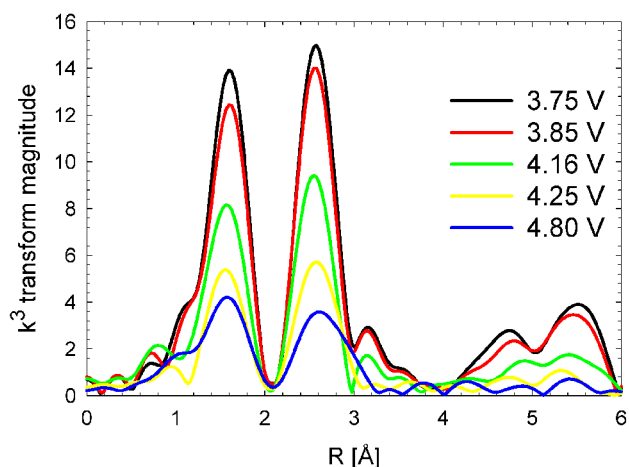


Figure 6. The Fourier transform of the EXAFS of Cr absorbers in a Cr-Mn based cathode material for representative states of charge.

XAS measurements clearly show that the mobility of the Cr ions between octahedral and tetrahedral sites is highly reversible, particularly after first charge. The finding that Cr, to a large extent, is the active metal undergoing oxidation/reduction rather than Mn is very interesting and unusual. Equally interesting are the high reversibility (at least after first charge) of the 3-electron oxidation/reduction process and the easy mobility of Cr between octahedral and tetrahedral sites. One of the remarkable aspects of this material is that two normally electrochemically inactive materials, LiCrO_2 and Li_2MnO_3 , when synthesized together in an intimate domain structure, produce a material that cycles reversibly with competitive capacities.

Acknowledgements

We thank Drs. I. Davidson, I. Kargina, K. Pandya, X. Sun, P. Whitfield and X.-Q. Yang for their help with the experiments and for their thoughtful suggestions. This work was supported by the Office of Advanced Automotive Technologies, U.S. DOE under contract number DE-AC02-98CH10886. The work was done under the auspices of the Advanced Technology Development Program and the Batteries for Advanced Transportation Technologies Program. Research carried out at the National Synchrotron Light Source, Brookhaven National Laboratory, which is supported by the U.S. Department of Energy, Division of Materials Sciences and Division of Chemical Sciences, under Contract No. DE-AC02-98CH10886.

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